NASA TT F-11,733

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GPO PRICE $ ____________

CSFTI PRICE(S) $ ____________

Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

Translation of "Polyvinyl Chloride no Bunshi Kozo To
Shyoseibutsu Tono Kankei"
Chemical Society of Japan,
Vol. 65. pp. 1617-1622, 1962

N68-30855	
(ACCESSION NUMBER)	(THRU)
12	1
(PAGES)	(CODE)
	06
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

FACILITY FORM 602

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON D.C. 20546 MAY 1968

ON THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE OF POLYVINYL CHLORIDE AND ITS THERMAL DECOMPOSITION PRODUCT[+]

*/1617

Sugiro Ohtani and Takeharu Ishikawa[**]

In order to investigate molecular structure of polyvinyl chloride and its thermal decomposition product, a thermal weight analysis of polyvinyl chloride was conducted and infrared and UV absorption spectra of the product obtained by heating at 425°C were observed. Polyvinyl chloride was Geon 103 EP(G) and polymerized at -30°C(F).

Activation energy of both materials obtained from the initial decomposition period of thermal weight analysis curve was 22 Kcal, but for the thermal decomposition process above 400°C, G was 37 Kcal and F, 46 Kcal. Both materials were separated into ~~few~~ several fractions by column chromatography and infrared and UV absorption spectra were investigated. The results were as follows. The average molecular weight of decomposition product was 700-800 and these were composed of ring structure and saturated ~~fat~~ aromatic family structure. The decomposition product from G had more ~~fat~~ aromatic family structure than that of F. F seemed to have more linear type ring compounds than G.

These results indicate that syndiotactic and isotactic structures in PVC play an important role in determining the structure of the decomposition product.

1. Introduction

Research on carbon compounds has been remarkably advanced recently and the trends are largely classified into two. One of them is physical treatment and the other is organic chemical treatment including polymeric material. As a result, composition and structure of raw material controlling the fundamental carbonization were much observed. However, the initial state of carbonization is not clear in many respects and the main factor controlling this process is not clearly known.

[+] This is Report No. 12. Research on Carbonization and Graphitization of Organic Compound.

[*] Numbers in the margin indicate pagination in the original foreign text.

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Interest in the change of polymeric material by heating in relation to thermal stability has increased considerably. Despite many researches on the subject, a sufficient basis for understanding initial process of carbonization is not available. In this report, the changes of low temperature polymerized polyvinyl chloride or commercial polyvinyl chloride during heating and its decomposition product at 425°C were observed. From the difference of these two, the degree of difference in the carbonization process, when the compositions are the same, but the structure is different, and decomposition products was investigated. We have already reported that the structure of commercial polyvinyl chloride decomposition product at 410-450°C contains ring structure and saturated fat family structure with an average molecular weight of 700 and discussed initial carbonization process of polyvinyl chloride. This report is based on these results. The reasons for using polyvinyl chloride as test material are as follows. (1) Structure of PVC is clearly known. (2) Yield of carbon material is large and research in this field is quite advanced. (3) The change during the initial process is well known compared with other polymeric materials and the decomposition product above 300°C is considered to be mainly pure hydrocarbon compound. (4) As already reported, there is a temperature range (410-480°C) where low molecular weight fraction, soluble in solvent, forms before carbonization of the decomposition products. Thus, it is possible to investigate decomposition products chemically.

2. Experimental results

2.1 Test material

The following two types of materials were used.

G: Commercial Geon 103 EP
F: Photo polymerization at -30°C.

Test material is reprecipitated from tetrahydrofuran solution using methanol. The structural difference of this material has already been discussed by Asahina[2] and Shimauchi[3]. According to their results, F has more syndiotactic structure than G. Figure 1 shows C-Cl stretch band of infrared spectrum for both materials. The measurement was conducted with the KBr disc method. Absorption at 605 cm^{-1} reported by Shimauchi was not observed, but β and γ absorption of α was large. F had more syndiotactic structure compared with G and some crystallinity was observed.

2.2 Weight loss and activation energy in nitrogen atmosphere

Using heat balance, weight loss was measured in a nitrogen atmosphere. The results are shown in Figure 2. The weight loss of G and F up to 350°C. Above 400°C, the weight loss is accompanied by melting and carbon structure[1] is formed around 500°C. Initial state of weight loss curve for both G and F is in complete agreement. The activation energy calculated from initial values between 220-275°C by the Freeman-Carroll method[4] is 22

Kcal. Also, the activation energy for decomposition product formed above 300°C was calculated from the curve between 410-450°C. This reaction is expected to include many kinds of reactions and the activation energy is the total of all the reactions. The activation energy for F is 46 Kcal and G, 37 Kcal, indicating that the value for G is slightly smaller.

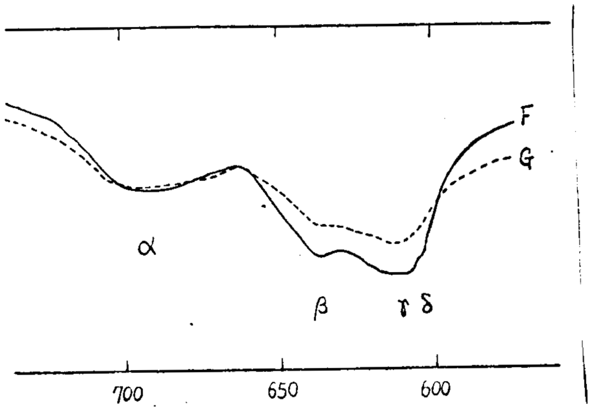


Figure 1 Infrared absorption spectra of PVC

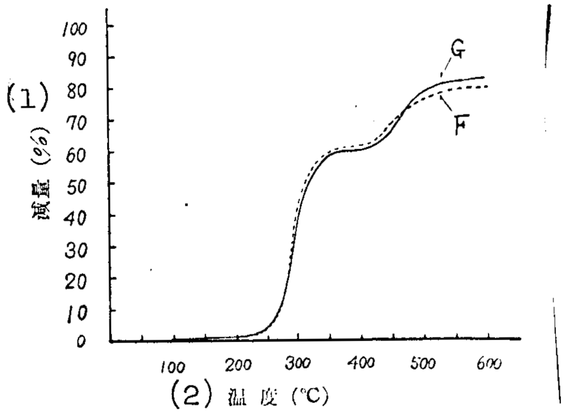


Figure 2 Weight loss curve of PVC in N_2 atmosphere
Heating rate ; 5°C/min

1. Weight loss (%)
2. Temperature (°C)

2.3. Separation of decomposition product at 425°C by chromatography

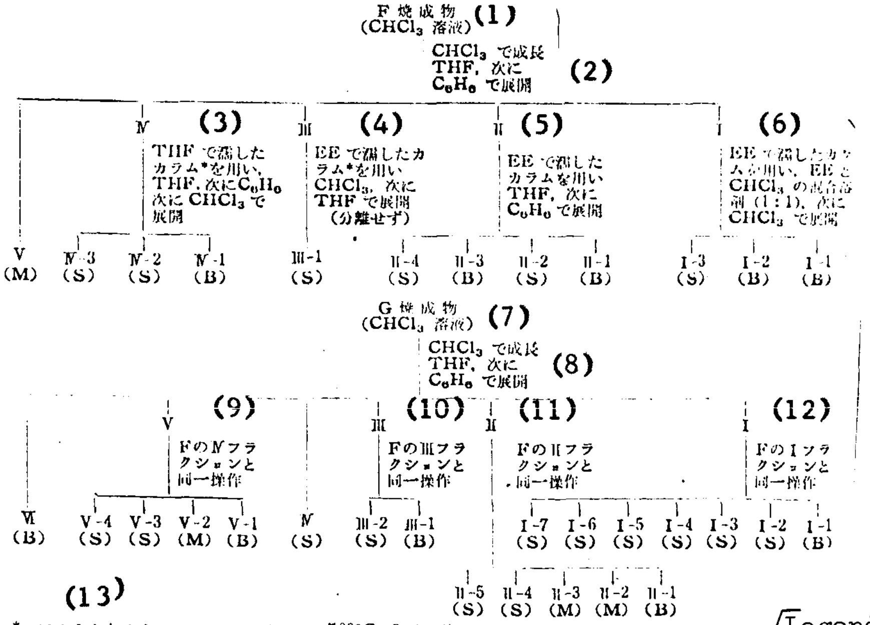
When PVC is heated in a nitrogen atmosphere, hydrogen chloride is liberated and polyene structure and cross-linking reaction produce a dark brown insoluble decomposition product like other decomposition products obtained from organic matter. However, in case of PVC decomposition above 410°C, the weak C-C bond is broken and low molecular weight material, soluble in various solvents, is formed. From the investigation of this decomposition product at the temperature indicated, we can presume the decomposition process or structure of decomposition products at lower temperatures. We have already investigated the thermal change of PVC by this method.[1,5] The separation of decomposition products by chromatography was not successful and the fractionation method was used. Since this method involves heating for a prolonged time, there is a danger of changing the nature of material. We have, therefore, attempted the chromatographical separation of decomposition products at 425°C. Initially, mixed solvents of cyclohexane and benzene (volume ratio 1:3) and cyclohexane and carbon tetrachloride (volume ratio 2:1) were used for two dimensional paper chromatography for comparison.

When the results are compared under ultraviolet rays, both materials have a diagonal type zone. And the difference was noted by the intensity of flourescent light. Since this method does not give sufficient separation and quantitative analysis after separation is not possible, column chromatography using alumina as the adoption agent was utilized for separation. After various elution agents were tested, the method shown in table I was used. Diameter of column is 30 mm and the test material is about 0.7 g.

Observing with ultraviolet light, the fraction with a large mobile ratio was eluted and the small mobile ratio was taken out after cutting the column. Solvent was removed from each fraction under reduced pressure. The solvent removal under reduced pressure was continued more than a day at room temperature and the residual matter was used in the experiment. Figure 3 shows the mobile ratio of each fraction and weight percentage against the original material. Total of each fraction is 95.5% and 93.6% for G.

Table 1

Conditions of chromatography and fractions

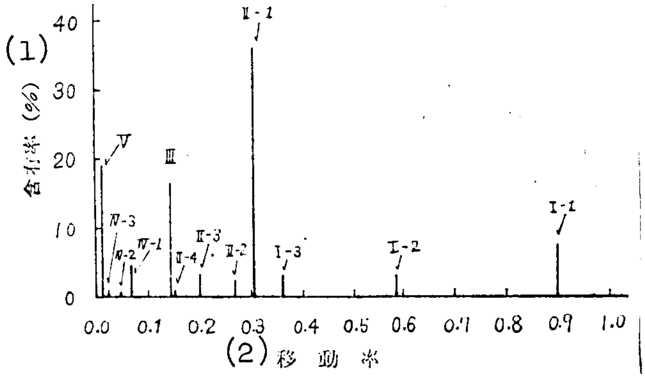

F 焼成物 (CHCl3 溶液) (1)
CHCl3 で成長 THF, 次に C6H6 で展開 (2)
Ⅳ (3)
THF で濡したカラム*を用い、THF, 次にC6H6 次に CHCl3 で展開
Ⅲ (4)
EE で濡したカラム*を用い CHCl3, 次に THF で展開 (分離せず)
Ⅱ (5)
EE で濡したカラムな用い THF, 次に C6H6 で展開
Ⅰ (6)
EE で濡したカラムを用い、EE と CHCl3 の混合溶剤 (1:1), 次に CHCl3 で展開
Ⅴ (M)
Ⅳ-3 (S)
Ⅳ-2 (S)
Ⅳ-1 (B)
Ⅲ-1 (S)
Ⅱ-4 (S)
Ⅱ-3 (B)
Ⅱ-2 (S)
Ⅱ-1 (B)
Ⅰ-3 (S)
Ⅰ-2 (B)
Ⅰ-1 (B)
G 焼成物 (CHCl3 溶液) (7)
CHCl3 で成長 THF, 次に C6H6 で展開 (8)
Ⅴ (9)
FのⅣフラクションと同一操作
Ⅲ (10)
FのⅢフラクションと同一操作
Ⅱ (11)
FのⅡフラクションと同一操作
Ⅰ (12)
FのⅠフラクションと同一操作
Ⅵ (B)
Ⅴ-4 (S)
Ⅴ-3 (S)
Ⅴ-2 (M)
Ⅴ-1 (B)
Ⅳ (S)
Ⅲ-2 (S)
Ⅲ-1 (B)
Ⅰ-7 (S)
Ⅰ-6 (S)
Ⅰ-5 (S)
Ⅰ-4 (S)
Ⅰ-3 (S)
Ⅰ-2 (S)
Ⅰ-1 (B)
Ⅱ-5 (S)
Ⅱ-4 (S)
Ⅱ-3 (M)
Ⅱ-2 (M)
Ⅱ-1 (B)
(13)

* アルミナをメチルアルコールで処理し, 100°C, 3 時間乾燥.
(S)：紫外線下で明瞭な幅の狭いフラクション, (B)：幅の広いフラクション,
(M)：(S) と (B) の中間のフラクション.
移動率の大きいフラクションから順に I, II, III‥, または 1, 2, 3‥ として示した.

/Legend on following page/

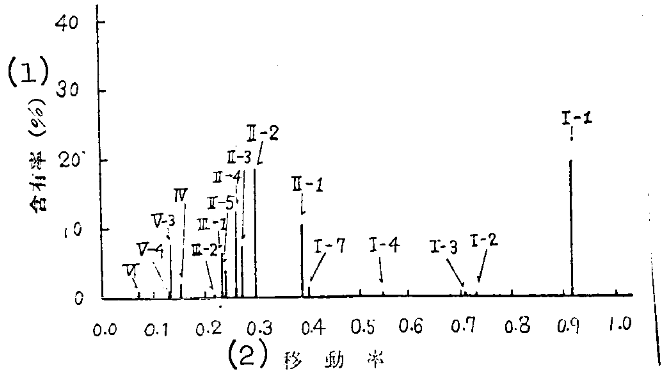
Legend:
1. Decomposition product F ($CHCl_3$ solvent)
2. Used $CHCl_3$, THF and then C_6H_6
3. Column is eluted with THF, C_6H_6 and then $CHCl_3$
4. Column is wetted with EE and eluted with $CHCl_3$ and then THF (no separation)
5. Column is wetted with EE and eluted with THF and then C_6H_6
6. Column is wetted with EE and eluted with mixed solvent of EE and $CHCl_3$ and then $CHCl_3$
7. Decomposition product F. ($CHCl_3$ solvent)
8. **Used $CHCl_3$, THF and C_6H_6**
9. Same as fraction F IV
10. Same as fraction F III
11. Same as fraction F II
12. Same as fraction F I
13. Alumina is treated with methyl alcohol and dried 3 hours at $100^{\circ}C$

(S): Narrow width fraction, (B): Fraction of wide width
(M): Fraction between (S) and (B)
Order of large mobile ratio was indicated by I,II, III, -- or 1,2,3 --



1. Inclusion ratio
2. Mobile ratio

Figure 3a Relationship Between Mobile Ratio of Each Fraction from F and Inclusion Ratio



1. Inclusion ratio
2. Mobile ratio

Figure 3b Relationship between mobile ratio of each fraction from G and inclusion ratio

Material G is largely classified into two groups, the fraction of mobile ratio 1.0-0.9 and 0.4-0.13. Material F has more of the fraction with mobile ratio 0.3 and others with 0.9, 1.5 and 0.02 exist more than material G.

2.4. Average molecular weight of each fraction

Average molecular weight of each fraction measured by Rust method is shown in Figure 4.

The amount of some fraction was too small to measure. Most of them were centered between 400-800 and its distribution was from 161 to 1140. Before chromatographical treatment, the average molecular weight of G is 700 and F 800.

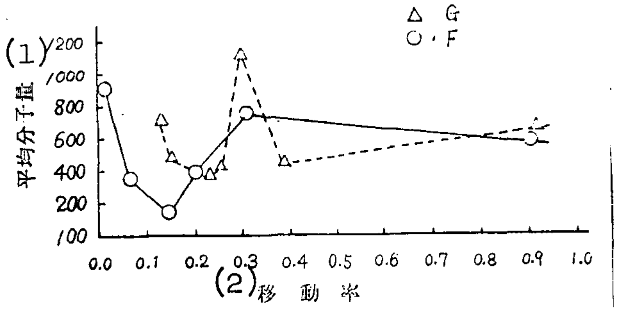


Figure 4 Average molecular weight of each fraction

1. Average molecular weight
2. Mobile ratio

2.5. Observation by infrared absorption spectrum

Before chromatographical separation, the decomposition product shows the following absorption.

3030, 2920, 2840, 1600, 1445, 1370, 880-860, 810, 740 cm^{-1}.

These absorptions have a width wider than pure materials. Each fraction separated by column chromatography gives a different absorption spectrum. Among the spectra, the difference is large in the 1800-1300 cm^{-1} and 900-700 cm^{-1} ranges. This is shown in Figure 5 and Figure 6 including inclusion ratio greater than 3%.

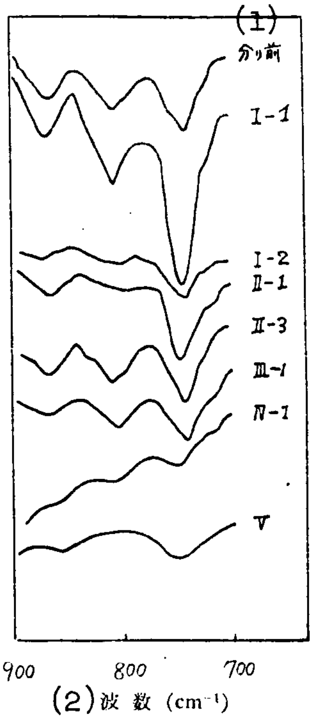


Figure 5 Infrared spectrum of F (900-700 cm^{-1})

1. Before separation
2. Wave length

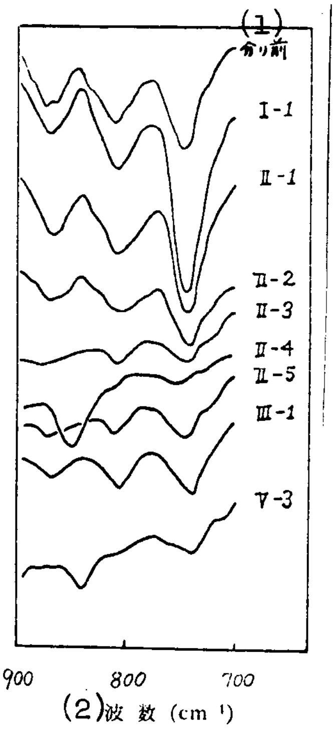


Figure 6 Infrared spectrum of G (900-700 cm^{-1})

1. Before separation
2. Wave length

Three absorption peaks between 900-700 cm^{-1}, i.e., 740, 810 and 870 cm^{-1}, are due to phenyl group δ C-H. Absorption at 740 cm^{-1} is when adjacent hydrogens are 4 or 5, at 810 cm^{-1} when adjacent hydrogens are 2 and at 870 cm^{-1} when adjacent hydrogen is only 1. Since absorption at 700 cm^{-1} is missing, the material is two ring compound rather than phenyl group. In such cases, the absorption at 810 cm^{-1} is either due to linear aromatic compounds or due to aromatic compounds of bent state such as phenanthren or cresen. As shown in Figure 5, II-1 (inclusion ratio 36%) and V-3 (8%) of F material consisting of 56% of fraction do not show the absorption at 810 cm^{-1}. The decomposition products have absorption at 2920 cm^{-1} and 1450 cm^{-1}, indicating the presence of considerable amounts of saturated fat structure. When this is combined with aromatic structure, the linear and nonlinear compounds are difficult to be classified by the presence or absence of 810 cm^{-1} absorption. However, the fractions of F material having 810 cm^{-1} absorption are 2.8 times more than G material. This seems to indicate that linear aromatic structure in decomposition products from F are more than the decomposition products from G.

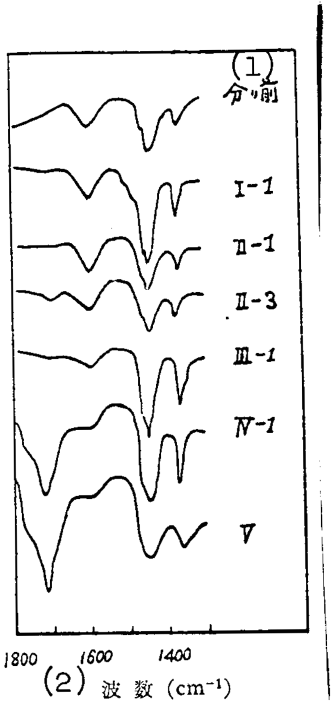


Figure 6a Infrared spectrum of decomposition products from F (1800-1300 cm^{-1})

1. Before separation
2. Wave length

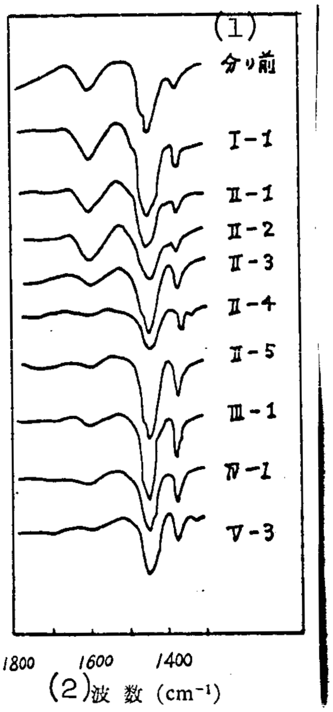


Figure 6b Infrared spectrum of decomposition products from G (800-1300 cm^{-1})

1. Before separation
2. Wave length

Intensity of 1445 cm^{-1} absorption and 1370 cm^{-1} absorption shown in Figure 6 is compared here. Intensity ratio of both absorptions obtained from the spectrum of each fraction, i.e., D_{1445} cm-1/D_{1370} cm-1, is 1.3-2.0 for each fraction of F material and 1.7-2.4 for each fraction of G material. In general, the value for F is smaller than the value for G. Since the KBr disc method is used here, it is difficult to compare quantitatively, but the inclusion ratio for CH_3 in decomposition product of F is larger than that of G. The length of the alkane side chain seems to be shorter for decomposition products of F. Comparing the intensity of 3060 cm^{-1} and 2920 cm^{-1} absorption, Darom -H/Daliph-H value is 0.19 for F and 0.13 for G, and the inclusion ratio of saturated fat against aromatic structure is larger for F than G.

Interpretation of infrared spectrum for a part of F material, i.e., IV-1 and V absorption at 1720 cm^{-1}, is very difficult. This absorption is absent in each fraction from G. The fractionated material was also the same as before. This is not observed in F material before chromatographical separation. This also can not be considered due to residual matter from the elution reagent. The absorption at 1720 cm^{-1} is probably due to change in material during chromatographical operation or unexpected contaminant.

Fractions IV-1 and V have medium absorption at 1180 cm^{-1} and 1040-1050 cm^{-1} and weak absorption at 3400 cm^{-1} in addition to 1720 cm^{-1}. The type of carbonyl group absorption at 1720 cm^{-1} can not be determined from these data, but considering the absence of 1300-1250 cm^{-1} absorption and the presence of absorption at a longer wave length than 1700 cm^{-1}, the carbonyl groups are not associated with aromatic structures such as quinone type or phenyl aldehyde type but are present in the alkane part.

2.6. Observation by ultraviolet light

According to ultraviolet spectrum, each fraction from both materials, F and G, is largely classified into three groups as shown in Figure 7.

The first group has maxima at 241-245 mμ and 258-265 mμ and absorption decreases rapidly at longer wave lengths (F-A group). The second group has maximum absorption at 268-270 mμ and absorption in the 240-300 mμ range (F-B group). The remaining group has maximum absorption at 250-245 mμ and the absorption is mildly curved until 350 mμ (F-C). In G material, there is a group similar to F-A having maximum absorption at 270 mu (G-A), a group having wider absorption spectrum than F-B (G-B group) and a group having maximum absorption at 260 mμ (G-C).

From the results of ultraviolet spectrum, each component does'nt seem to be sharply fractionated although the separation method is different from the previous method.

Thus, we can only presume the degree of aromatic structure in the main component from this result. The present measurement made it possible to include the wave length down to 240 mμ. And we were able to distinguish the fractions with or without 245 mμ absorption peak and the relatively similar spectra obtained previously were clearly separated into three large groups. As described earlier, carbonyl groups of F material are not associated with aromatic structure but is part of the alkane structure. Therefore, the influence of these carbonyl groups on ultraviolet absorption spectra is considered to be very small. This is also clear from the fact that both, G and F, have very similar spectrums and no influence of carbonyl groups was detected. The results of Figure 7 imply that 245 mμ absorption of F-A and G-A is tetradecahydrocorronen 7 type associated with the carbonization process. The overall shape of the spectrum is similar to the piren type indicated by Dudenstel[8], and it is supposed that antracene derivatives, phenanthrene and crysen were added to the overall spectrum. In B group, there is small difference between G and F, but the main components consist of anthracene, tetracene, phenanthrene and crysen having maximum absorption at 250-270 mμ. The A-C group have mainly anthracene type, having maximum absorption at 250 mμ and B-C group triphenylene, 9, 10-dimethyl anthracene type anthracene derivative and phenanthrene having maximum absorption near 260 mμ. These are considered to be the materials containing various 3-4 ring aromatic structures. Using the average molecular weight of each fraction, the molar absorption coefficient at maximum wave length is calculated. The value of log ε is 3.8-4.5. Considering the presence of the alkane part, the value for the 3-4 ring aromatic structure is very reasonable.

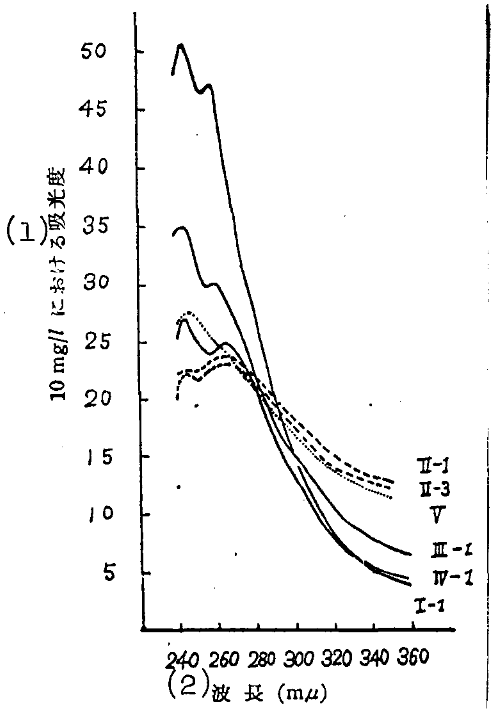


Figure 7a Ultraviolet absorption spectrum of decomposition product from F (chloroform solvent)

1. Intensity per 10 mg/l
2. Wave length

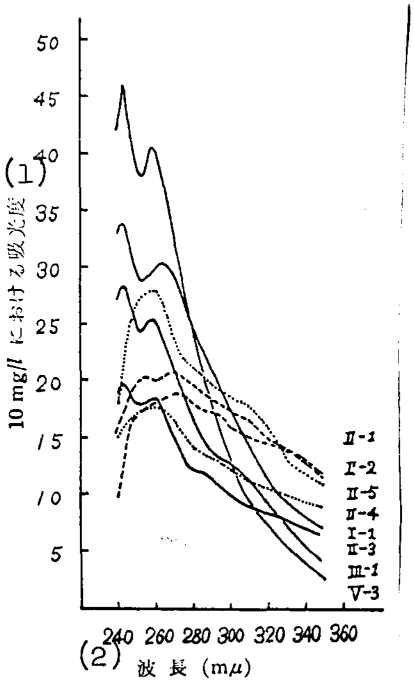


Figure 7b Ultraviolet spectrum of decomposition product from G

1. Absorption intensity per 10 mg/l
2. Wave length

3. Discussion

The results are summarized as follows.

(1) Weight loss curve for both materials agree during initial period of decomposition, and activation energy of 22 Kcal was obtained.

(2) Weight loss of F above 400°C is smaller and the calculated activation energies for F and G are 46 Kcal and 37 Kcal, respectively.

(3) Column chromatography using alumina was attempted, and the material was separated into more fractions than by the previous method.

(4) The following was observed from infrared spectrum.

(a) The decomposition products consist of an aromatic part and a saturated fat part.

(b) Considering the absorption intensity ratio at 1445 cm^{-1} and 1370 cm^{-1}, F has less fat part.

(c) About 56% of fractions from F and 20% from G have no absorption at 810 cm^{-1} or weak absorption.

(d) Carbonyl group absorption is observed in F material, probably resulting from chromatographical operation and as a part of alkane near 1720 cm^{-1}.

(5) In ultraviolet spectra, both materials are largely classified into three groups corresponding to a 3-4 ring aromatic family.

(6) The average molecular weight of F is 800 and G 700.

As mentioned earlier, it is reasonable to say from these results that the decomposition products of both F and G have the basic structure of few ring aromatic family. Examination of the differences between two on the basic structure makes it possible to suppose the influence of syndiotactic and isotactic structure on initial carbonization process below 425°C and subsequent carbonization. From the above summarized facts, the following can be considered. There is no difference in activation energy for the initial decomposition period during the reaction of hydrogen chloride liberation, but the difference is observed in thermal decomposition above 400°C. This indicates that a difference exists in the decomposition product by hydrogen chloride liberation and bridge combination between the molecules or the aromatization reaction is related to molecular structure of raw material. This point agrees with summary (4) a, b, and c. The side chain of F decomposition product is shorter than G decomposition product or the saturated fat connecting aromatic compounds is small in F material. Thus, F decomposition product is thermally more stable. We have already mentioned that the generation of fat structure is based on bridge combination between molecules. Thus, the amount or length of fat structure is directly related to this bridge combination. Also, the mode of intermolecular reaction appears as the difference in aromatic structures. According to the research of Shimauchi, et al[3], the most stable form of syndiotactic PVC is the zigzag type and in the case of isotactic, the helix formed by repetition of trans and gache is the most stable. The probability of forming linear type aromatic structure by combining two molecules in zigzag form is extremely large, whereas the probability of forming helix is very small. But the probability of forming helix by combining more than three molecules is larger than the zigzag type. Therefore, the difference in the amount of syndiotactic and isotactic structure is the cause for indicating the result of (4) in summary.

In a little more detail, the case of crystalline or noncrystalline syndiotactic structure and influence of side chain branching should be considered, but it is not possible to discuss more than the above from the present facts.

The low temperature polymerized PVC was provided by the Kureha Kasei Tokyo Research Center. We wish to thank Mr. Hare and other members for their cooperation.

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Received May 7, 1962